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STERIC EFFECTS IN ALPHA-OLEFIN REACTIVITY

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, 1/Lt David W. Thomson, project engineer.

This report covers work accomplished from November 1962 to June 1963.

The author wishes to gratefully acknowledge the assistance of Dr. M. S. Newman of the Ohio State University in this project.

ABSTRACT

Addition reactions to the double bond of a series of sterically-hindered alpha-olefins have been carried out. The kinetics of these reactions were measured and the rates of reaction correlated with the steric effects present in the olefin. A theory known as "Newman's rule of six" has been successfully applied to alpha-olefins to correlate reaction rates with steric effects and to explain, in part, the difficulty of obtaining desirable polymers from these olefins.

This technical documentary has been reviewed and is approved.

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
AF Materials Laboratory

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INTRODUCTION

Of all the factors that influence the formation of a high-molecular-weight polymer, probably the least understood is the effect of steric factors which may be present in the monomer. In addition, the steric effects which influence the normal addition of a reagent to the double bond of an alpha-olefin have not been studied. The purpose of the present work was to observe and measure the steric effects in a conventional addition reaction to the double bond of a series of hindered alpha-olefins. With the successful completion of this first step, an attempt would be made to apply an existing theory to explain the results and, in part, the difficulty of obtaining high-molecular-weight polymers from these same olefins.

The concept of steric hindrance dates back to the previous century. Numerous reviews have appeared which cover both the progress made in the area and the correlation of the effects of steric hindrance to specific systems (References 1 and 2). However, with the refinements of the resonance theory and the emphasis placed on inductive effects, the role of steric hindrance has received less attention in recent work.

Addition Reactions to Olefins

Addition reactions to olefins have received considerable attention, both in organic and polymer chemistry research. An excellent series of papers by Robertson (Reference 3) is illustrative of olefin research in the field of physical-organic chemistry. Both the kinetics and mechanisms of the addition reactions of halogens and halogen acids to a series of olefins were studied. However the olefins, for the most part, contained other polar groups within the molecule and the purpose of the work was to observe and correlate the inductive effects of these groups with reactivity. When simple unsubstituted olefins were studied (Reference 4), little or no steric effects were noted and the data were interpreted in terms of the inductive and hyperconjugative effects. A study in which only steric factors are involved has not been made on addition reactions of simple olefins.

Increased emphasis has been given to alpha-olefin research in the area of polymer chemistry. With the purpose of extending the knowledge obtained from vinyl polymers, studies have been carried out on the polymerization reactions of higher straight- and branched-chain alpha-olefins (References 5 and 6). In the majority of cases, the reactions do not go to completion, giving low-molecular-weight noncrystalline polymers. Usually, no explanation has been given for the results although one author (Reference 6) hints that the poor results may be due to steric factors.

Peracids as Reagents

The reaction of an unsaturated compound with an organic peracid gives, in many cases, a quantitative yield of the corresponding epoxide (Reference 7). Epoxidation reactions on unsaturated compounds have been attempted using reagents such as peracetic, performic, and particularly perbenzoic acid. The latter is especially suited to this reaction due to its ease of preparation, experimental procedures, and the near-quantitative yield of the epoxide which is obtained. Peracetic and performic acids tend to produce the epoxides as intermediates but often proceed further to yield the corresponding glycols and hydroxyacetates.

The use of perbenzoic acid in the quantitative determination of unsaturation has been refined by Kolthoff (Reference 8). Recently, this reaction has been applied to kinetic studies as a classical addition reaction to the double bond (Reference 9). Numerous studies have verified the existence of second-order kinetics, first order with respect to both olefin and perbenzoic acid (Reference 10). A great deal of confusion still exists as to the true mechanism of a peracid reaction and a brief survey of peracid reactions will be presented here.

In 1899, Baeyer and Villiger (References 11 and 12) reported the preparation of a series of lactones and acetates by the reaction of ketones with peracids. This work was subsequently clarified by Robertson and Waters (Reference 13). The basic reaction involved the insertion of an oxygen atom next to the carbonyl group.

$$CH_3 - \underset{\underset{O}{\|}}{C} - R \; + \; H_2SO_5 \longrightarrow CH_3 - \overset{\overset{O}{\|}}{C} - OR \; + \; H_2SO_4$$
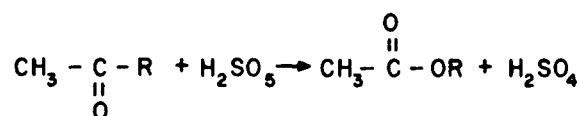
Although the exact mechanism of this reaction is in doubt, Robertson and Waters (Reference 13) definitely established that an ionic mechanism was taking place. Since the oxygen atom was always inserted in the same place, the formation of free hydroxyl radicals was ruled out. Friess (Reference 14) found that the rates of peracid reactions were increased when carried out in more-polar solvents, which is evidence for an ionic mechanism. The proposed reaction mechanism is based largely on the postulated ionization products of the peracid.
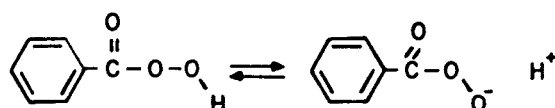
If this is the correct ionization scheme for the peracid, the reaction is simply an acid-catalyzed addition to the carbonyl group of the ketone, followed by a rearrangement to the product.

Under acidic conditions, an olefin will react with perbenzoic acid to give a ketone according to the following reaction (Reference 15):
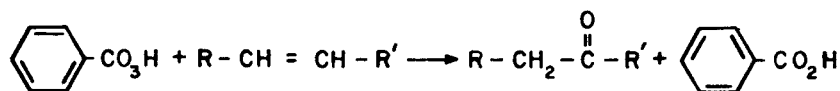
The postulated mechanism for this reaction is based on a different ionization product for peracids (Reference 16). The proposed ionization products for perbenzoic acid in a polar solvent are:
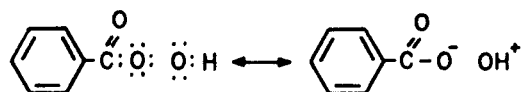
It is postulated that the hydroxyl cation attacks the double bond, followed by expulsion of a proton and rearrangement (Reference 15).

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$$R-CH=CH-R' \xrightarrow{OH^+} R-CH \overset{\frown}{\underset{\underset{H}{O^+}}{CH}}-R' \xrightarrow{-H^+}$$

$$R-CH=\underset{\underset{OH}{|}}{C}-R' \longrightarrow R-CH_2-\underset{\underset{O}{\|}}{C}-R'$$
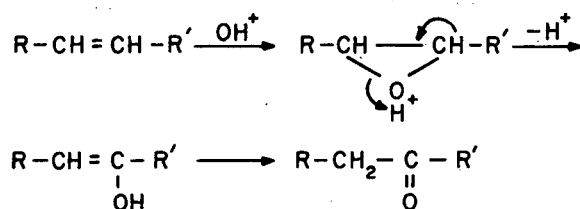
In addition to the evidence for an ionic mechanism, the majority of peracid reactions in polar solvents have been found to be subject to general acid catalysis (References 13, 14, and 17).

The mechanism for epoxidation reactions of olefins is not well defined. Almost all epoxidation reactions have been found to give exclusively the cis-epoxide. This striking stereospecificity of the reaction essentially rules out the formation of a free carbonium ion as the intermediate. This has led Swern (Reference 18) to postulate the formation of an initial peracid-general acid complex which reacts with the olefin according to the following scheme:

$$R-CH \overset{\frown}{\underset{O}{\qquad}} CH-R' + R''-CO_2H + HA$$

where HA represents the general acid which catalyzes the reaction. This mechanism has been found to be more acceptable, especially for reactions carried out in less-polar solvents.

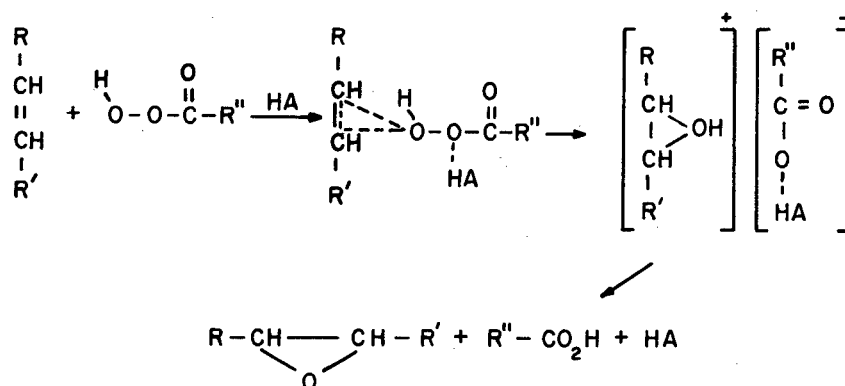However, results of epoxidation reactions carried out in non-polar solvents such as benzene and ether indicate that other mechanisms may be favored. Many peracid reactions, in solvents of low polarity, are not subject to general acid catalysis (References 9 and 10). Good yields of the epoxides are obtained and the reactions appear to proceed at a normal rate. These results led Lynch and Pausacker to postulate the initial formation of an olefin-peracid complex as the slow step. A subsequent rearrangement of the electrons results in the formation of the epoxide and benzoic acid, according to the following scheme:

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The application of epoxidation reactions to olefinic systems has been quite extensive. Excellent reviews on the scope of the reaction have been published (References 7 and 19). In a study of epoxidation reactions using performic acid, Swern (Reference 20) found that the speed of reaction with a series of olefins was much less than with carboxylic acids derived from the same olefins. This was explained as resulting from the reduced solubility of the olefins in the solvent, formic acid. When the same study was carried out using peracetic acid as the reagent, the differences in reaction speed were even more pronounced.

When the kinetics were determined for the reactions of a few simple olefins with peracetic acid (Reference 21), the results showed that the relative rates of reaction were essentially constant between similar structures. When hydrocarbon groups were substituted on either the olefinic carbon atoms or the carbon atom adjacent to the double bond, a marked increase in rate was observed. This was explained with the assumption that the peroxide oxygen is electrophilic in character and is readily released by the peracid. Thus, substituted alkyl groups would increase the nucleophilic character of the double bond and therefore increase the rate of reaction. No steric effects were observed in these reactions.

Newman's Rule of Six

In 1950, in an attempt to place the role of steric hindrance on a more meaningful basis, Newman (Reference 22) proposed his theory regarding the rule of six. If the atoms in an organic acid are numbered consecutively starting with the carbonyl oxygen as one, the feature present in butyric acid and higher homologs that is absent in the lower members is the presence of atoms in the six position.

$$
\begin{array}{c}
O_1 \qquad\quad H_6 \\
\| \qquad H_6 \backslash | \\
HO - C \qquad\qquad C - H \\
\ _2 \ \backslash C - C \ / \ _5 \quad _6 \\
\ _3 \quad _4
\end{array}
$$

This led Newman to propose the following empirical rule: "In reactions involving addition to an unsaturated function, the greater number of atoms in the six position, the greater will be the steric effect." This rule is known as the rule of six. Of course, branching on the alpha-carbon is a contributory factor to the steric effect and must be considered when applicable.

The same rule of six may easily be applied to alpha-olefins. If the atoms are numbered, starting with the farthest unsaturated carbon atom as one, the system is perfectly analagous to the acids.

$$
\begin{array}{c}
R_6 \\
| \\
R_6 - C - C - C - C = C \\
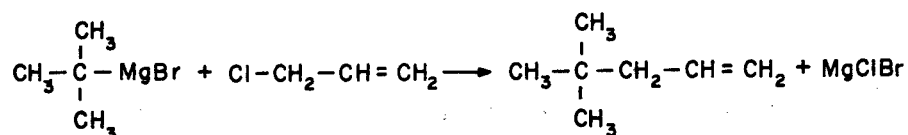\ _6 \ |_5 \ _4 \ _3 \ _2 \ _1 \\
R_6
\end{array}
$$

4

By adding a reagent across the double bond, in this case perbenzoic acid, the steric effects of atoms in the six position should be observed readily. Inasmuch as many isolated facts in the literature, observed with a variety of systems, can be explained by the application of the rule of six (Reference 22), a logical extension to hindered alpha-olefins should prove fruitful. The promise of identifying and measuring these steric effects prompted the undertaking of the present work.

EXPERIMENTAL*

Preparation of Olefins
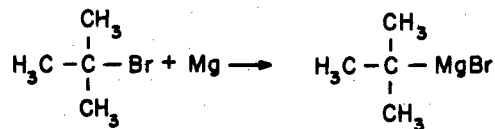
4,4-Dimethyl-1-pentene

4,4-Dimethyl-1-pentene was prepared by the Grignard coupling of allyl chloride with t-butylmagnesium bromide according to the method of Whitmore (Reference 23).

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-MgBr + Cl-CH_2-CH=CH_2 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH=CH_2 + MgClBr$$

The following experimental procedure was used. In a three-necked one-liter flask, equipped with stirrer, thermometer, addition funnel, and cooling bath, were placed 66 g (0.86 mole) of allyl chloride and 100 ml of anhydrous ether. The solution was cooled to -10°C and 10 ml of a 1.05 M solution of t-butylmagnesium bromide in ether (total volume 425 ml.) was slowly added. The reaction began immediately and the remainder of the solution was added during a three-hour period over a temperature range of -5 to 0°C. Following the addition, the reaction mixture was stirred at room temperature for three hours. The presence of excess Grignard reagent was confirmed by the Gilman color test (Reference 24) and the reaction mixture was poured over crushed ice. An orange-colored ether solution separated which was washed with ammoniacal ammonium sulfate and dried over anhydrous calcium chloride. The ether solution was then decanted, filtered, and fractionated through a 26-inch long by 7/8-inch diameter saddle-packed column under a nitrogen atmosphere. Approximately 50 ml of a clear liquid was obtained which, upon refractionation, gave 49.2 g (60%) of 4,4-dimethyl-1-pentene, b.p. 71-72°C (from Reference 23, lit. b.p. 71-72°C).

t-Butylmagnesium Bromide

This reagent was prepared from t-butyl bromide and magnesium according to the method of Kharasch (Reference 25).

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + Mg \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-MgBr$$
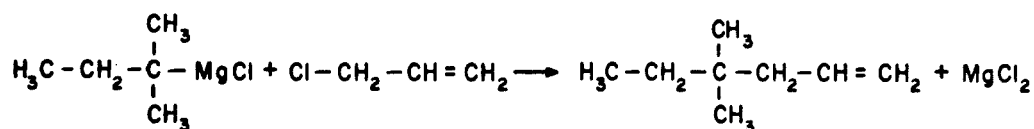
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*All boiling points reported are uncorrected.

In a one-liter three-necked flask, equipped with addition funnel, stirrer, reflux condenser, and heating mantle, were placed 36.7 g (1.5 moles) of magnesium turnings and three small crystals of iodine. The flask was then heated with a small flame to activate the magnesium. After cooling, 30 ml of a solution of 178 g (1.3 moles) of t-butyl bromide in 200 ml of anhydrous ether was added slowly. The reaction began immediately and the reaction mixture was then diluted with 100 ml of anhydrous ether and brought to reflux. The remainder of the ether solution was then added at the rate of one drop per second. Upon completion of the addition, the heating was stopped and the mixture stirred for one hour, filtered, and standardized.* The solution contained 1.05 moles (81%) of Grignard reagent per liter.
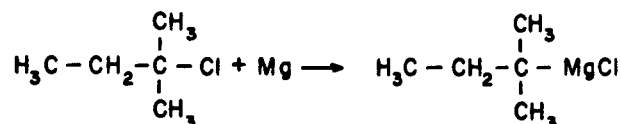
4,4-Dimethyl-1-hexene

4,4-Dimethyl-1-hexene was prepared by the Grignard coupling of allyl chloride with t-amylmagnesium chloride.

$$H_3C-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-MgCl + Cl-CH_2-CH=CH_2 \longrightarrow H_3C-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH=CH_2 + MgCl_2$$

In a one-liter three-necked flask, equipped with stirrer, condenser, and addition funnel, was placed 106 g (1.4 moles) of allyl chloride. The flask was cooled to 0°C and 10 ml of a 1.56 M ether solution of t-amylmagnesium chloride (total volume 500 ml)·was added to initiate the reaction. The reaction began immediately and the remainder of the solution was added at the rate of one drop per second with the temperature being maintained at 0°C throughout. The reaction mixture was stirred for an additional two hours and poured over ice. The ether layer which separated was washed twice with ammoniacal ammonium sulfate, once with water, and dried over anhydrous calcium chloride. The ether was then evaporated and the remaining liquid fractionated through a 26-inch long by 7/8 inch diameter saddle-packed column under a nitrogen atmosphere. The yield of 4,4-dimethyl-1-hexene (b.p. 107°C) was 68 g (61%), lit b.p. 107°C (Reference 26).

t-Amylmagnesium Chloride

This reagent was prepared by the reaction of t-amyl chloride with magnesium.

$$H_3C-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + Mg \longrightarrow H_3C-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-MgCl$$

To a one-liter three-necked flask, equipped with stirrer, addition funnel, and condenser, were added 49 g of magnesium turnings and several small crystals of iodine. The flask was heated with a small flame until the magnesium was activated. After cooling, 75 ml of a solution of 213 g (2.00 moles) of t-amyl chloride in 250 ml of anhydrous ether was slowly added. The reaction mixture was slowly brought to a reflux and the remainder of the ether solution added at the rate of one drop per second. Following the addition, the reaction mixture was diluted with 200 ml of anhydrous ether and stirred an additional three hours.

---

*Standardization of the Grignard solutions was accomplished by titration of a 10 ml-aliquot in water with standard hydrochloric acid. Phenolphthalein was used as the indicator.

Standardization of the Grignard solution was carried out as before. The solution contained 1.56 moles (78%) of Grignard reagent per liter.

Commercial Samples

Samples of the following olefins were obtained from commercial sources: 1-butene, 1-pentene, 1-decene, and 4-methyl-1-pentene.

Purification of Olefins

Prior to use, all olefins except 1-butene were fractionated through a 26-inch long by 7/8 inch diameter saddle-packed column in a nitrogen atmosphere. Constant boiling fractions were taken which were correlated with the respective index of refraction.

TABLE I

PHYSICAL CONSTANTS OF ALPHA-OLEFINS

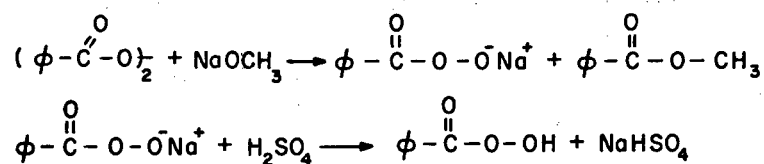| OLEFIN	B.P. °C	N_D^{20}
1-butene[*]	—	—
1-pentene	30	1.3715[**]
1-decene	171	1.4295[**]
4-methyl-1-pentene	54	1.3838[**]
4,4-dimethyl-1-pentene	73	1.3916[**]
4,4-dimethyl-1-hexene	107	1.4103[**]

[*] Obtained pure - purity checked by VPC
[**] Within 0.0003 units of reported literature value

In addition, all olefins were characterized by the use of vapor-phase chromatography. 0.01 ml samples were analyzed in a F & M Model 500 Programmed High Temperature Gas Chromatograph. Helium was used as the carrier gas through a six-foot silicone gum rubber on Chromasorb P column. The most impure of the olefins, 1-butene, showed the amount of impurity to be one part in 2276.

Preparation of Perbenzoic Acid

Perbenzoic acid was prepared by the action of sodium methoxide on benzoyl peroxide according to the method of Braun (Reference 27) as modified by Kolthoff (Reference 8).

$$(\phi - \overset{O}{\overset{\|}{C}} - O \overset{}{\underset{2}{}} + NaOCH_3 \longrightarrow \phi - \overset{O}{\overset{\|}{C}} - O - \bar{O} Na^+ + \phi - \overset{O}{\overset{\|}{C}} - O - CH_3$$

$$\phi - \overset{O}{\overset{\|}{C}} - O - \bar{O} Na^+ + H_2SO_4 \longrightarrow \phi - \overset{O}{\overset{\|}{C}} - O - OH + NaHSO_4$$

In a 500 ml three-necked flask was placed 100 ml of absolute methanol. With cooling, 5.2 g of metallic sodium was added and the resulting solution cooled to -5°C. A solution of 50 g (0.21 mole) of benzoyl peroxide in 200 ml of anhydrous chloroform was added slowly with stirring. The temperature was maintained at -5°C throughout the addition.

Following the addition, 150 ml of ice water was added to the reaction mixture and the resulting solution poured over crushed ice. The chloroform layer was then separated and the aqueous layer washed with 100 ml portions of carbon tetrachloride. The aqueous layer was then acidified with 225 ml of 1 N sulfuric acid, liberating the perbenzoic acid. The perbenzoic acid was then extracted with spectroquality benzene, and the solution was dried over anhydrous sodium sulfate at 10°C. This solution was then diluted to one-liter volume with spectroquality benzene.

Standardization of the perbenzoic acid solution was accomplished using the method given by Swern (Reference 28). Aliquots (5.00 ml) were pipeted into flasks containing 50 ml of 0.4 N acetic acid and 1 g of potassium iodide. The resulting solution was mixed thoroughly and titrated with 0.1 N sodium thiosulfate to a starch end point. The solution contained 0.129 moles of perbenzoic acid per liter.

Apparatus

Constant Temperature Bath

A four-gallon glass jar was set in a larger cardboard box and exploded mica was packed into the empty spaces for insulation. The top of the mica was covered with a thick layer of paraffin wax.

Water was used as the bath fluid.

An efficient air-driven stirrer was mounted in the bath. To maintain a 30°C temperature, a 125-watt knife heater was placed near the stirrer. The heater was controlled by a Fischer differential mercury thermoregulator. The temperature was controlled to ± 0.02°.

Microburet

A Fischer 10 ml microburet was used for the titrations.

Procedure of an Experimental Run

The experimental procedure and the method for treatment of data for the epoxidation reactions were taken from the work of Lynch and Pausacker (Reference 9).

The epoxidation reactions of the olefins were carried out in the following manner. The olefin (ca 2-3 x 10^{-3} mole) was weighed into a 50 ml volumetric flask which was then placed in the constant temperature bath. After two hours, a solution of perbenzoic acid (ca 6-8 x 10^{-2} molar) also at 30°C was added to the mark and the resulting solution mixed thoroughly. Aliquot portions (5.00 ml) were withdrawn at determined times and added to a solution consisting of 5.00 ml of 0.5 N potassium iodide and 10.00 ml of 2.0 N sulfuric acid. The liberated iodine was titrated with 0.1 N sodium thiosulfate to a starch end point. No less than five determinations were made during each experimental run. The reactions were followed to approximately 40 percent completion.

CALCULATIONS AND RESULTS

Treatment of Data

The two variables measuring the reaction are time and the disappearance of starting materials, both olefin and perbenzoic acid. The second was chosen as the unit of time. For experimental convenience, it was decided to work in terms of the disappearance of perbenzoic acid. The original concentrations of the olefins were determined by weight while the original concentration of perbenzoic acid was determined volumetrically.

Rate Constants

The calculations of the rate constants are based on the method of Lynch and Pausacker (Reference 9). The reaction representing the epoxidation of an olefin by perbenzoic acid is:

$$R - CH = CH - R' + \phi CO_3H \longrightarrow R - CH \overset{}{\underset{O}{\diagdown\diagup}} CH - R' + \phi CO_2H \tag{1}$$
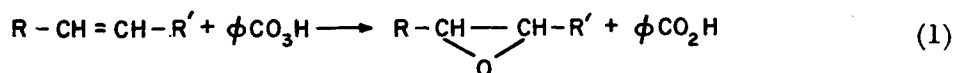
and the rate of disappearance of benzoic acid is expressed by the second-order relationship:

$$\frac{- d(\phi CO_3H)}{dt} = k(R - CH = CH - R')(\phi CO_3H) \tag{2}$$

The general equation for a second-order reaction, first-order with respect to each reactant A and B, is given by the expression (Reference 29):

$$\frac{1}{B_0 - A_0} \ln \frac{A_0 B}{B_0 A} = kt \tag{3}$$

where A_0 and B_0 represent the original concentrations of the reactants and B and A are their concentrations at time t. For the reaction of an olefin with an excess of perbenzoic acid, the equation can be written:

$$\frac{1}{Pb_0 - O_0} \ln \left[(\frac{O_0}{Pb_0})(\frac{Pb}{O}) \right] = kt \tag{4}$$

where Pb_0 and O_0 represent the original concentrations (molarity) of perbenzoic acid and olefin respectively.

At this point a simplification of the calculations and resulting equations can be made. Since the determination of perbenzoic acid at time t is performed by titration with thiosulfate (0.1 N), this concentration is already in terms of milliliters of sodium thiosulfate. If the original concentrations of perbenzoic acid and olefin are now calculated in terms of their thiosulfate equivalents (ml), Equation 4 reduces to:

$$\frac{1}{c'} 2.3 \log \left[(\frac{x}{x-c})(\frac{O_0}{Pb_0}) \right] = kt \tag{5}$$

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where

$c = Pb_o - 0_o$ in ml of sodium thiosulfate

$c' = c$ in moles/liter

$x = P_b$ concentration at time t in ml of thiosulfate.

k = rate constant in liters mole^{-1} second^{-1}.

t = time in seconds

The value of x/x-c at time t is calculated and log x/x-c is plotted versus t. The straight line which is obtained verifies the second-order reaction. The slope is calculated from two points on the graph and the value of the rate constant, k, is obtained from the following relationship:

$$\text{SLOPE} = \left(\frac{c'}{2.303} \right) k \tag{6}$$

where c' has the same meaning as before. The value for c' is obtained from the following equation:

$$c' = \frac{c_{ml} \times 1/2 \times M_{Na_2S_2O_3}}{5\text{-ml aliquot}} \tag{7}$$

This method was used for all calculations. Duplicate determinations on the same olefin gave values for k which agreed within 3 percent. Table 2 shows the results of the epoxidation of the olefins.

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TABLE 2

KINETICS OF EPOXIDATION OF ALPHA-OLEFINS

| COMPOUND | STRUCTURE | SIX NUMBER | NATURE OF ATOMS IN SIX POSITION | | $k \times 10^{-4}$ | $k^{*}_{avg} \times 10^{-4}$ | $\dfrac{k_{butene}}{k_{olefin}}$ | $\% \Delta k^{**}$ |
			C	H				
I – butene	C–C–C=C	0	0	0	25.28 24.71	2 5	1.00	2.3
I – pentene	–C–C–C–C=C	3	0	3	10.32 10.35	10.34	2.42	0.3
I – decene	C₁₀H₂₀	3	1	2	9.29 9.56	9.43	2.65	2.9
4 – methyl – I – pentene	–C–C–C–C=C / –C–	6	0	6	6.89 6.76	6.83	3.66	1.9
4,4 – dimethyl – I – hexene	–C– / C–C–C–C–C=C / –C–	9	1	8	4.63 4.70	4.66	5.37	0.2
4,4 – dimethyl – I – pentene	–C– / –C–C–C–C=C / –C–	9	0	9	4.55 4.63	4.59	5.44	1.8

* The average k-value of duplicate determinations, in liters mole^{-1} second^{-2}

** The percent difference between the k-values obtained from duplicate determinations

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DISCUSSION

The selection of alpha-olefins to be included in this study was governed by two factors. Only hydrocarbons were selected in hopes of eliminating all electronegativity effects which might influence the reaction rates. In addition, substitution of methyl groups on the hydrocarbon chain was restricted to the carbon atom at least two positions away from the double bond. This was done in hopes of minimizing and/or holding constant any inductive effects or changes in hyperconjugation from the new groups.

As can be seen from Table 2, the k-values obtained from the respective olefins fall into an order which would be predicted from the rule of six. The k-value for 4,4-dimethyl-1-hexene is essentially equal to that of 4,4-dimethyl-1-pentene. This indicates that, when mono-substituted ethylenes reach a six number of nine, the steric factors cannot be distinguished. The distinction here between carbon and hydrogen atoms in the six positions is not possible, while the two olefins with a six number of three clearly show this difference. The differences in k-values between the respective olefins are small but are believed to be significant. In comparing these small differences to the larger differences obtained in the studies on acid esterification (Reference 22), it must be pointed out that a different experimental environment exists in the present case. If the mechanism for this reaction is truly ionic, then low reaction rates would be expected in anhydrous benzene solutions, and these small differences in rates of reaction would be a direct measure of the steric effects only.

If the reaction mechanism is three-centered, as proposed by Lynch and Pausacker (Reference 9), the differences obtained in rates would also appear to be a true measure of the steric effects.

Thus, it can be seen that, in general, the olefins with the greater six number react less readily and that the application of the rule of six to alpha-olefin reactivity appears to be justified.

Although a mechanism study was not intended in this work, the results obtained indicate that the reaction could not proceed by an ionic mechanism under the existing experimental conditions. The addition of an organic acid, benzoic acid, to one of the determinations with 4-methyl-1-pentene did not change the rate of the reaction. This is evidence that, under these conditions, general acid catalysis does not occur.

In terms of polymer formation, the results have shown conclusively that steric factors exert a large influence on the reactivity of the double bond. It would appear that this effect would also be observed in the rates of polymerization of these olefins, whether by free-radical or ionic mechanisms. With the fivefold decrease in reaction rate that was observed in the change from zero to nine atoms in the six position, ample opportunity would be provided for various chain-terminating and molecular-weight-limiting processes to occur.

Finally, the rule of six should be directly applicable to polymerization reactions as well as to simple addition reactions to help predict the ease of reaction and the resulting molecular weights of the polymers.

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APPENDIX

DATA AND GRAPHS

OF

EPOXIDATION REACTIONS

TABLE 3

EPOXIDATION OF 4,4-DIMETHYL-1-PENTENE

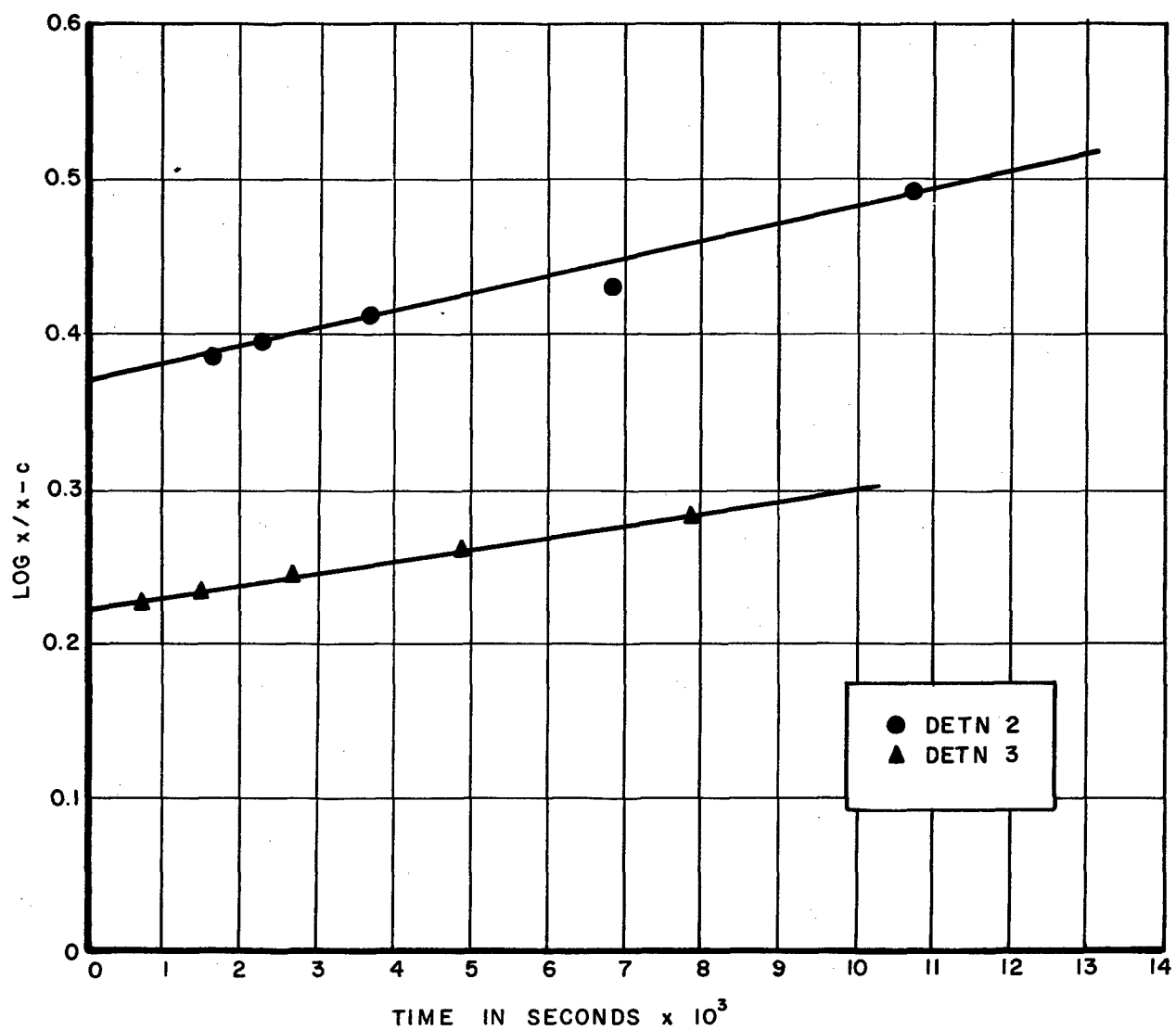|	TIME(sec)	ml 0.103 N $Na_2S_2O_3$	x/x-c	log x/x-c
DETN 2				
	1560.1	9.23	2.42	0.384
	2306.0	9.05	2.49	0.396
	3609.8	8.83	2.58	0.412
	6769.6	8.63	2.68	0.428
	10708.0	8.01	3.08	0.486
	14351.3	7.62	3.45	0.538
	wt olefin = 0.2119 g			
	std of perbenzoic acid = 9.60 ml 0.103 N $Na_2S_2O_3$/5ml soln			
DETN 3				
	644.1	9.14	1.69	0.228
	1434.7	9.02	1.70	0.230
	2600.0	8.70	1.75	0.243
	4860.3	8.28	1.82	0.260
	7816.4	7.76	1.92	0.283
	wt olefin = 0.2954 g			
	std of perbenzoic acid = 9.56 ml 0.103 N $Na_2S_2O_3$/5ml soln			
	k_2 = 4.55 x 10^{-4} liters mole^{-1} second^{-1}			
	k_3 = 4.63 x 10^{-4} liters mole^{-1} second^{-1}			
	k_{avg} = 4.59 x 10^{-4} liters mole^{-1} second^{-1}			
	%Δk = 1.8			

Figure 1. Epoxidation of 4, 4-Dimethyl-1-pentene Log x/x-c vs Time

TABLE 4

EPOXIDATION OF 4,4-DIMETHYL-1-HEXENE

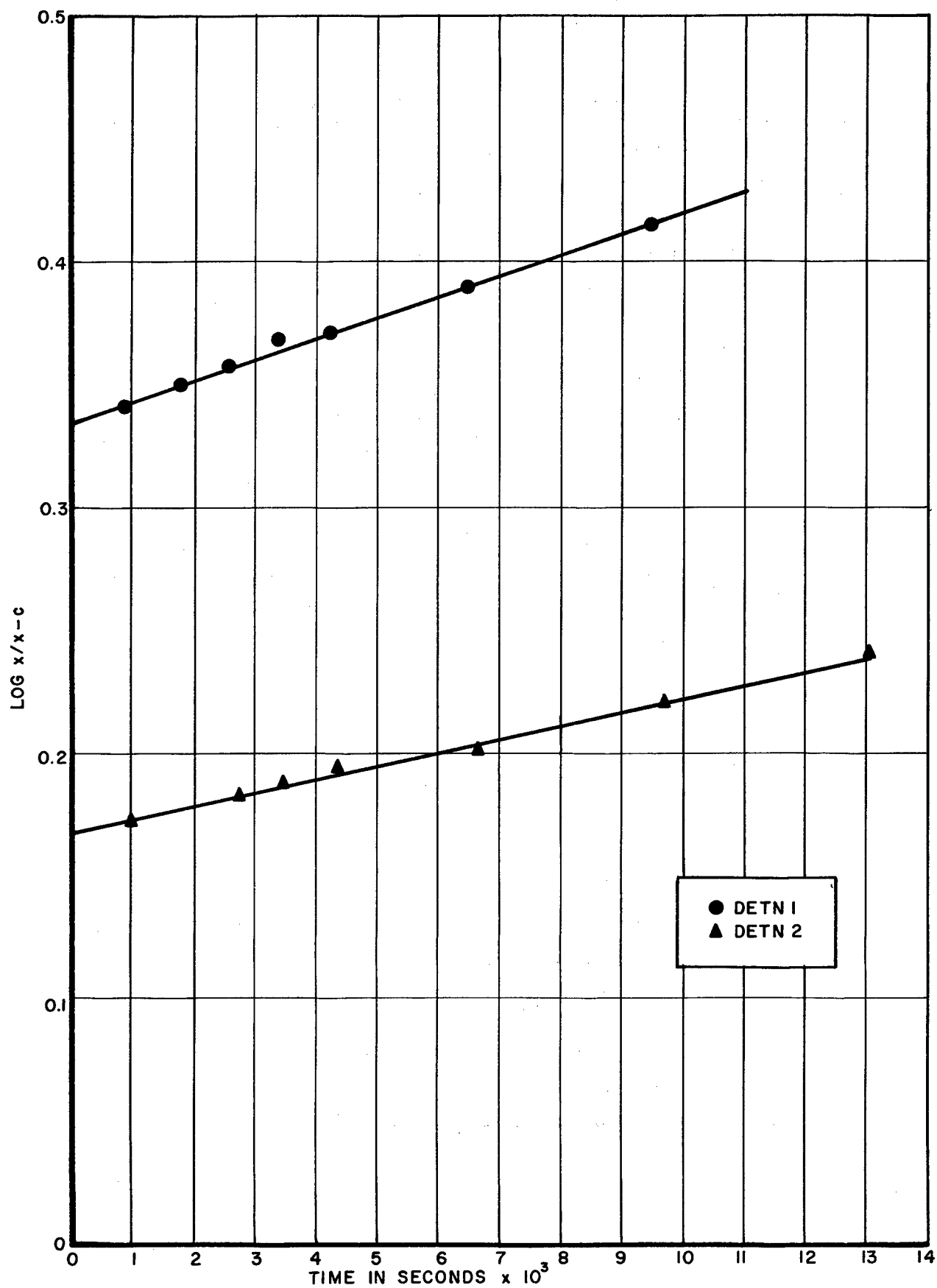|	TIME (sec)	ml 0.102 N $Na_2S_2O_3$	x/x-c	log x/x-c
DETN 1				
	803.7	7.34	2.19	0.341
	1739.7	7.23	2.23	0.349
	2563.1	7.11	2.28	0.358
	3329.0	6.98	2.33	0.368
	4219.0	6.95	2.35	0.371
	6433.0	6.74	2.45	0.389
	9467.2	6.48	2.60	0.415
	12824.9	6.16	2.84	0.453
	wt olefin = 0.2055g			
	std of perbenzoic acid = 7.58 ml 0.102 N $Na_2S_2O_3$/5ml soln			
DETN 2				
	978.1	7.27	1.49	0.172
	2716.7	6.94	1.52	0.182
	3463.4	6.79	1.54	0.188
	4376.1	6.62	1.56	0.193
	6611.4	6.44	1.59	0.200
	9707.2	5.98	1.66	0.220
	13041.6	5.63	1.73	0.239
	wt olefin = 0.2875 g			
	std of perbenzoic acid = 7.58 ml 0.103 N $Na_2S_2O_3$/5 ml soln			
	k_1 = 4.63 x 10^{-4} liters mole^{-1} second^{-1}			
	k_2 = 4.70 x 10^{-4} liters mole^{-1} second^{-1}			
	k_{avg} = 4.66 x 10^{-4} liters mole^{-1} second^{-1}			
	% Δk = 0.2			

Figure 2.   Epoxidation of 4,4-Dimethyl-1-hexene Log x/x-c vs Time

TABLE 5

EPOXIDATION OF 4-METHYL-1-PENTENE

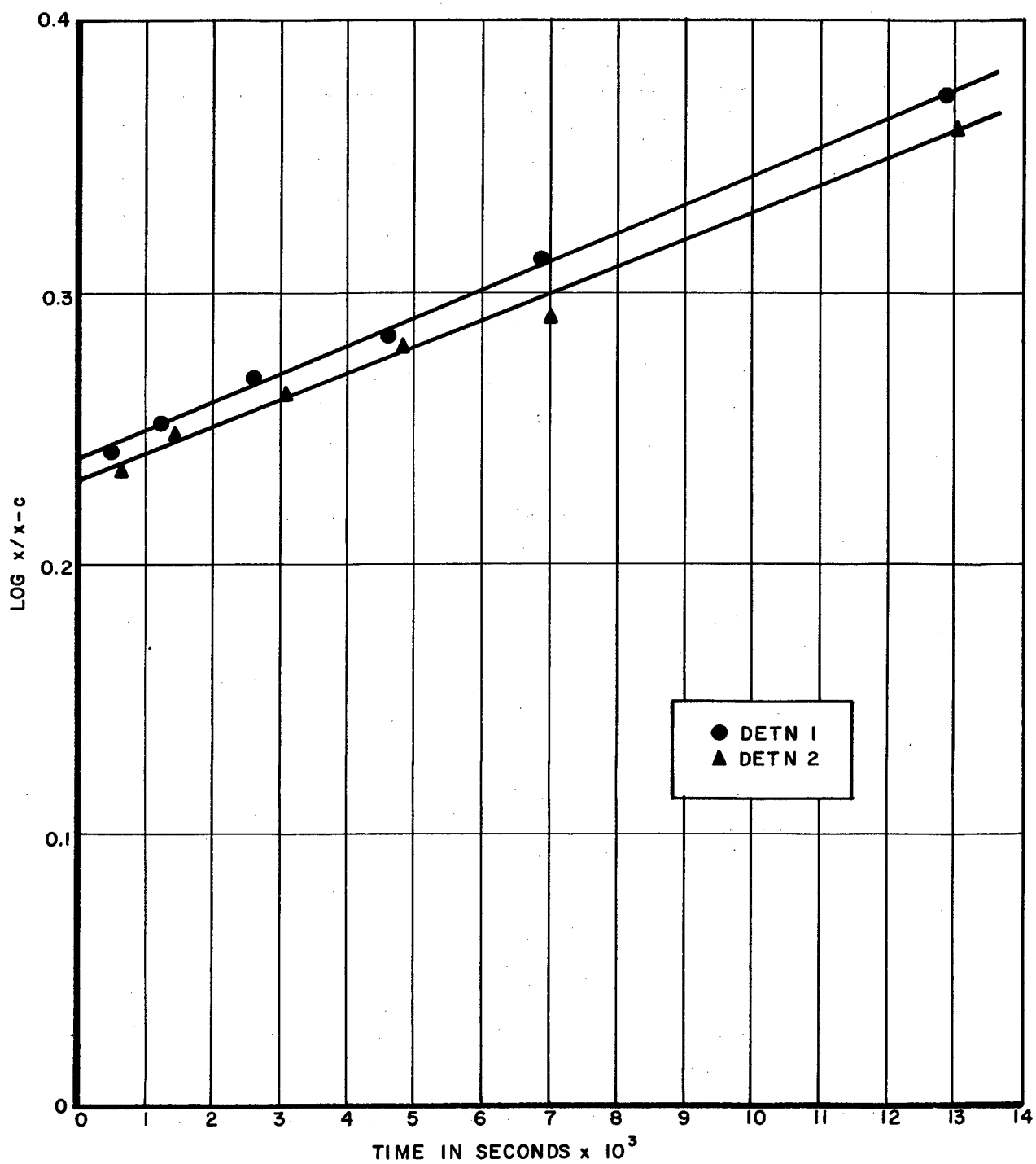|	TIME (sec)	ml 0.103 N $Na_2S_2O_3$	x / x-c	log x / x-c
DETN 1				
	489.3	7.41	1.56	0.193
	1240.4	7.12	1.59	0.201
	2579.2	6.80	1.64	0.215
	4599.4	6.47	1.69	0.228
	6874.3	6.06	1.78	0.250
	12911.3	5.36	1.98	0.297
	wt olefin = 0.2191 g			
	std of perbenzoic acid = 7.70 ml 0.103 N $Na_2S_2O_3$/5ml soln			
DETN 2				
	668.4	7.44	1.54	0.188
	1403.9	7.08	1.58	0.199
	3072.6	6.77	1.62	0.210
	4824.7	6.43	1.68	0.225
	7056.3	6.28	1.71	0.233
	13063.4	5.38	1.94	0.288
	wt olefin = 0.2216 g			
	std of perbenzoic acid = 7.70 ml 0.103 N $Na_2S_2O_3$/5ml soln			
	k_1 = 6.89 x 10^{-4} liters mole^{-1} second^{-1}			
	k_2 = 6.76 x 10^{-4} liters mole^{-1} second^{-1}			
	k_{avg} = 6.83 x 10^{-4} liters mole^{-1} second^{-1}			
	% Δk = 1.9			

Figure 3. Epoxidation of 4-Methyl-1-pentene Log x/x-c vs Time

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TABLE 6

EPOXIDATION OF 1-DECENE

	TIME (sec)	ml 0.101 N $Na_2S_2O_3$	x/x−c	log x/x−c
DETN 6				
	629.6	9.32	2.88	0.459
	1615.7	9.09	3.02	0.480
	2275.2	8.82	3.22	0.508
	3695.4	8.57	3.44	0.537
	7276.2	7.97	4.22	0.625
	wt olefin = 0.2640g			
	std of perbenzoic acid = 9.80 ml 0.101 N $Na_2S_2O_3$ / 5 ml soln			
DETN 7				
	810.8	9.34	2.68	0.428
	1771.0	9.01	2.86	0.456
	2476.7	8.72	3.05	0.484
	3813.9	8.50	3.22	0.508
	7429.3	7.85	3.94	0.596

wt olefin = 0.2788 g

std of perbenzoic acid = 9.80 ml 0.101 N $Na_2S_2O_3$ / 5 ml soln

k_6 = 9.29 x 10^{-4} liters $mole^{-1}$ $second^{-1}$

k_7 = 9.56 x 10^{-4} liters $mole^{-1}$ $second^{-1}$

k_{avg} = 9.43 x 10^{-4} liters $mole^{-1}$ $second^{-1}$

% Δk = 2.9

22
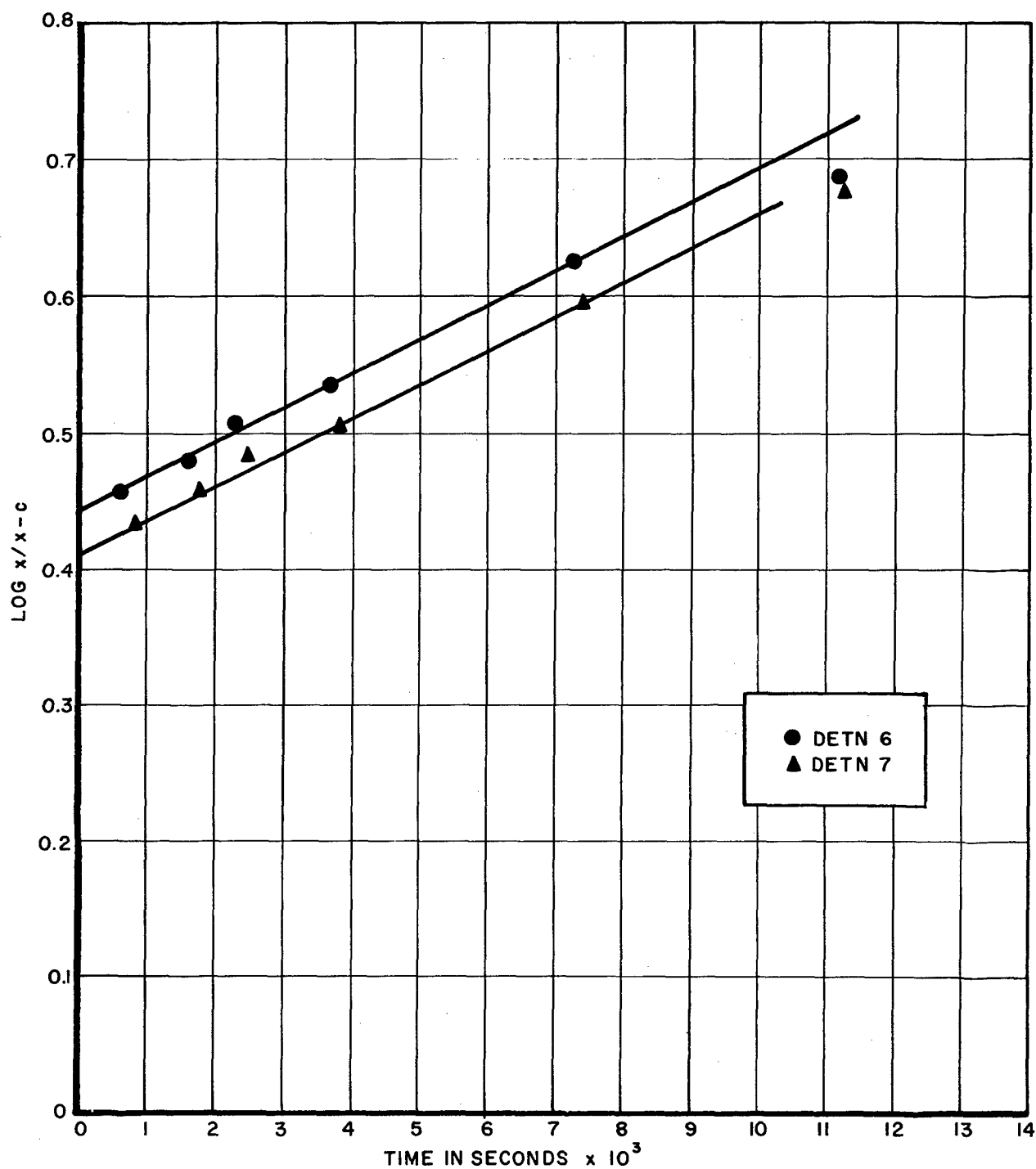
Figure 4. Epoxidation of 1-Decene Log x/x-c vs Time

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TABLE 7

EPOXIDATION OF 1-PENTENE

	TIME (sec)	ml 0.103 N $Na_2S_2O_3$	x/x−c	log x/x−c
DETN 1				
	1137.4	7.11	1.33	0.124
	1876.2	6.89	1.34	0.128
	2879.0	6.56	1.37	0.136
	4264.4	6.24	1.39	0.144
	7031.1	5.32	1.49	0.174
	9706.9	4.94	1.55	0.191
	wt olefin = 0.2147 g std of perbenzoic acid = 7.70 ml 0.103 N $Na_2S_2O_3$ / 5 ml soln			
DETN 2				
	1001.9	7.14	1.54	0.188
	1724.3	7.01	1.56	0.193
	2772.0	6.56	1.62	0.210
	4162.1	6.14	1.69	0.228
	6900.9	5.65	1.80	0.255
	9874.6	5.18	1.94	0.288
	wt olefin = 0.1876 g std of perbenzoic acid = 7.70 ml 0.103 N $Na_2S_2O_3$/5 ml soln			

$k_1 = 10.32 \times 10^{-4}$ liters mole^{-1} second^{-1}

$k_2 = 10.35 \times 10^{-4}$ liters mole^{-1} second^{-1}

$k_{avg} = 10.34 \times 10^{-4}$ liters mole^{-1} second^{-1}

% Δk = 0.3
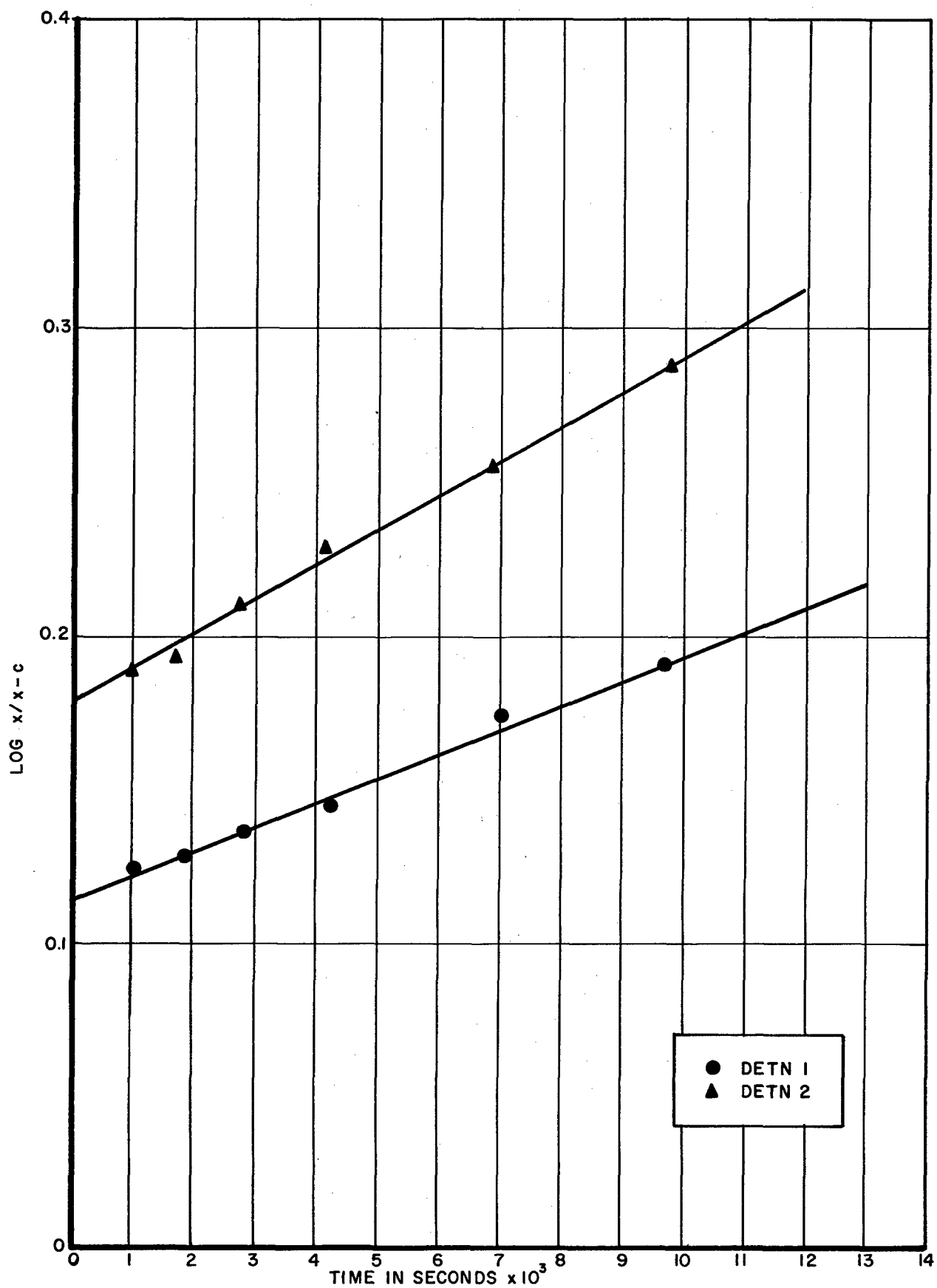
Figure 5. Epoxidation of 1-Pentene Log x/x-c vs Time

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TABLE 8

EPOXIDATION OF I- BUTENE

|	TIME (sec)	ml 0.102 N $Na_2S_2O_3$	x / x- c	log x / x- c
DETN I				
	608.7	4.09	I.32	0.122
	2123.4	3.63	I.38	0.140
	3081.I	3.43	I.41	0.150
	4158.0	3.28	I.44	0.158
	5327.0	3.21	I.45	0.162
	wt olefin = 0.1637g			
	std of perbenzoic acid = 7.70 ml 0.102 N $Na_2S_2O_3$/ 5ml soln			
DETN 4				
	1698.0	3.68	2.30	0.362
	2243.0	3.57	2.40	0.380
	3249.7	3.46	2.51	0.399
	3558.0	3.41	2.56	0.409
	6049.2	3.32	2.68	0.428
	wt olefin = 0.1013g			
	std of perbenzoic acid = 7.70 ml 0.102 N $Na_2S_2O_3$/5 ml soln			
	$k_1 = 25.28 \times 10^{-4}$ liters mole^{-1} second^{-1}			
	$k_4 = 24.71 \times 10^{-4}$ liters mole^{-1} second^{-1}			
	$k_{avg} = 25.00 \times 10^{-4}$ liters mole^{-1} second^{-1}			
	% Δk = 2.3			
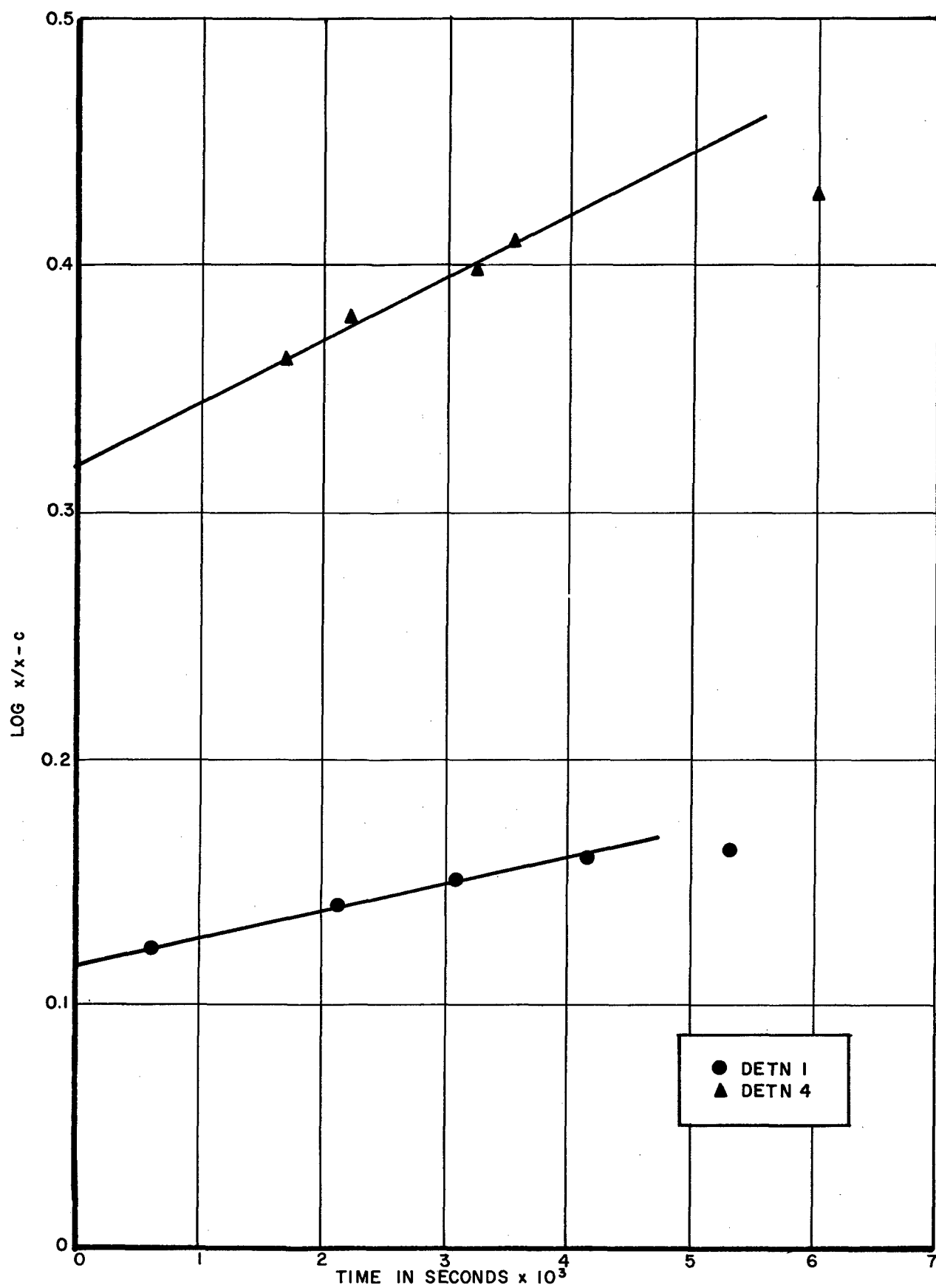
Figure 6. Epoxidation of 1-Butene Log x/x-c vs Time

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